Indian Journal of Pure & Applied Physics
Vol. 49, June 2011, pp. 398-400

Non-radiative energy transfer from Tb^{3+} to Ho^{3+} ions in zinc phosphate glass

Charu Ch Dhondiyal[1]*, B C Joshi[2], D K Upreti[3] & Bhawana Khulbey[4]

[1]Department of Physics, Govt P G College Uttarkashi (Uttarakhand), India

[2,3,4]Department of Physics, Kumaun University, S S J Campus, Almora (Uttarakhand), India

*E- mail: charu_dhondiyal@yahoo.co.in

Received 18 October 2010; revised 28 February 2011; accepted 17 March 2011

Steady state emission of terbium (Tb^{3+}) with varying concentration of holmium (Ho^{3+}) in zinc phosphate glass has been studied. Decrease in emission intensity of Tb^{3+} with increasing Ho^{3+} concentration indicates a non-radiative energy transfer from Tb^{3+} to Ho^{3+}. The energy transfer mechanism, energy levels of Tb^{3+} and Ho^{3+} involved in energy transfer and other parameters necessary for the quantitative study e.g. energy transfer efficiencies, transfer probabilities, critical transfer distance etc. have been computed.

Keywords: Non-radiative energy transfer, Zinc phosphate glass, Fluorescent spectra, Luminescence Sensitization, Rare earth ions

1 Introduction

The luminescence of rare earth ions in glass has been a subject of renewed interest since the advent of laser. Due to small oscillator strength, RE ions cannot absorb a significant portion of excitation energy. In order to obtain high luminescent efficiency, the phosphors doped with these ions (acceptor) can be co-activated with the help of some other ions (sensitizer) which absorbs an appropriate amount of excitation. Sensitizer transfers some of its excitation energy to the ion under study and consequently, the emission or efficiency of the later is enhanced. Many theories have been evolved out to understand the mechanism of energy transfer[1-5].

The terbium ion is well known for its relatively large absorption among rare earth ions and has bright green emission. Therefore, it is a suitable choice for sensitizing other RE ions. Much work has been done taking terbium as the energy donor in various hosts with an aim to transfer its excitation energy to other rare earth ions[6-9]. Joshi *et al*[6]. reported diffusion limited energy transfer at low Ho^{3+} concentration and electric dipole-dipole interaction at higher concentration. Yamashita and Ohisi observed energy transfer between Tb^{3+} to Yb^{3+} in borosilicate glass and found that co-operative energy transfer efficiency increases with increased doping concentration[8]. Joshi *et al.*[9] observed a non-radiative energy transfer from Tb^{3+} and Er^{3+} in zinc phosphate glass.

The present paper aims to find out the mechanism of energy transfer between Tb^{3+} and Ho^{3+} in zinc phosphate glass and quantitative measurements for transfer probability and transfer efficiencies.

2 Experimental Details

Sodium dihydrogen phosphate 2-hydrate ($NaH_2PO_4.2H_2O$) (E-Merck, India) and reagent grade zinc oxide (ZnO)(Ferak Berlin, Germany) were mixed in a proportion of 3:1 by weight respectively to prepare the host glass matrix. The rare earths chosen for the work were terbium oxide (Tb_4O_7, 99.9% pure) and holmium oxide (Ho_2O_3, 99.9% pure) obtained from GTE Sylvania, USA. Pure as well as rare earth doped glass samples (pallets of almost equal geometry and surface area) were prepared in an electric furnace at about 1213 K as described elsewhere[10].

The emission spectra were taken by steady state excitation of the samples with the 365 nm group of mercury lines obtained from a medium pressure mercury lamp having Wood's filter. A fluorometer using grating monochromator (CEL Model, HM104) dispersion 3.3 nm mm^{-1}, Czerny turner mounting, with a photomultiplier tube (RCA1P21) and a nanometer were used to scan the spectra.

3 Results and Discussion

The energy level diagrams of Tb^{3+} and Ho^{3+} are shown in Fig. 1. However, only terbium ion gives their characteristic emission in the visible region when excited by 365 nm group of mercury lines. Excited terbium ion in zinc phosphate glass decays rapidly to the metastable $^5D_4$ level. The emission spectra (uncorrected) of terbium ion (Fig. 2) shows 4 peaks at about 488, 542.5, 585.5, 626 nm because of the following transition $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_3$, respectively. The emission from $^5D_3$ level of Tb^{3+} was not observed in our system (1 wt% Tb^{3+}).

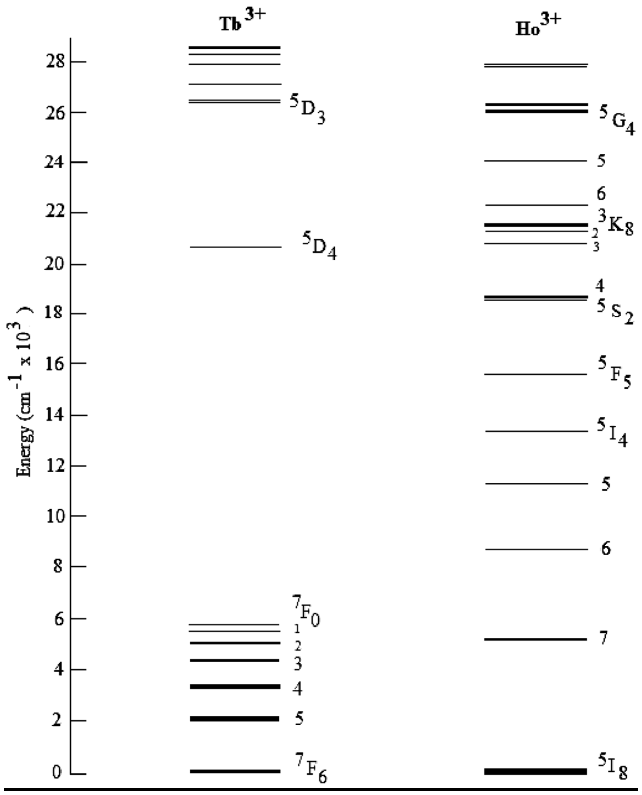

Fig. 1 — Energy level diagrams of Tb^{3+} and Ho^{3+}

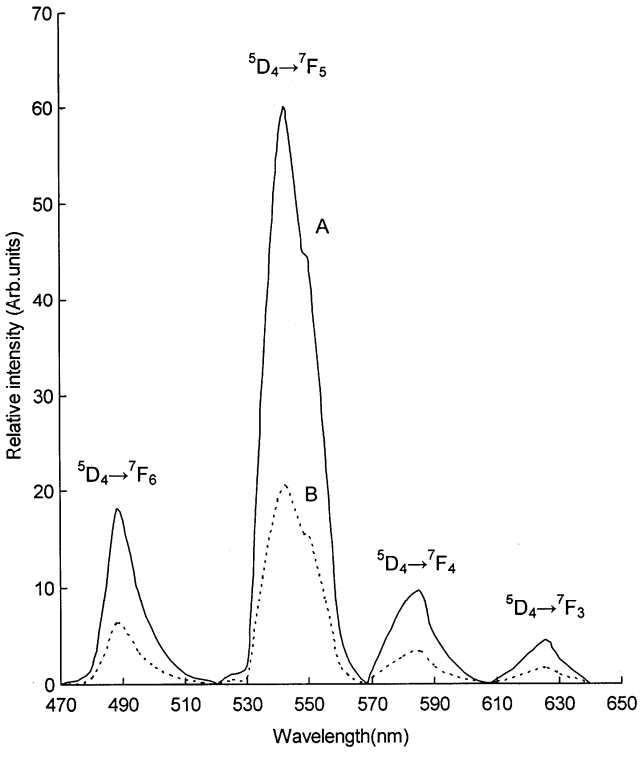

Fig. 2 — Emission spectra (uncorrected) of (A) Tb^{3+}(1.0 wt. % fixed) (B) Tb^{3+} (1.0 wt. %) +Ho^{3+} (1.0 wt %)

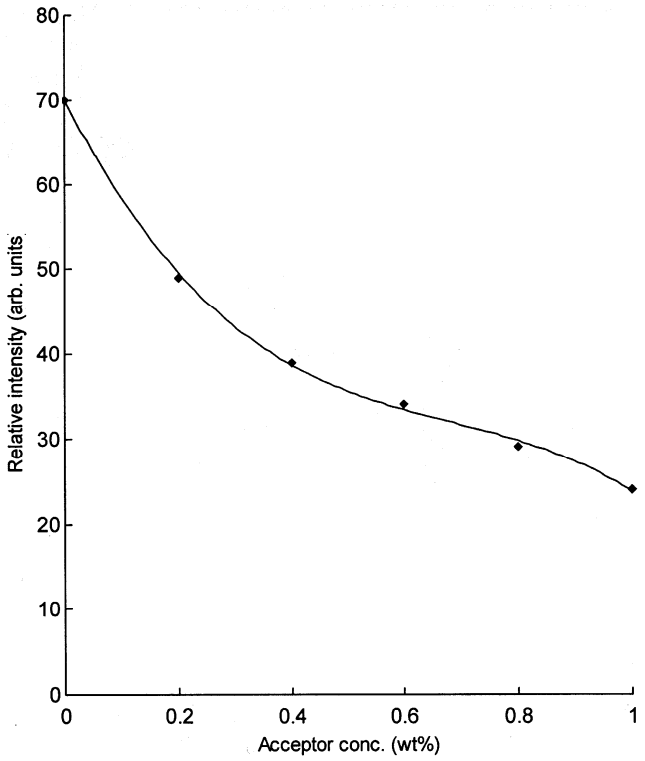

Fig. 3 — Emission intensity of Tb^{3+} (1.0 wt. %) in the presence of varying concentrations of Ho^{3+}

The reason of this may be the terbium ions make pairs (Tb-Tb) and because of this the excitation energy of the $^5D_3$ level relaxes to the $^5D_4$ level by cross-relaxation. Another possible reason for this may be due to fast relaxation from $^5D_3$ level since its lifetime is very small.

The uncorrected spectra of Tb^{3+} (1 wt% fixed) and the mixture of Tb^{3+} and Ho^{3+} (1 wt% each) are shown in Fig. 2 (A & B). A comparison of these two curve clearly shows that the intensity of emission of donor ion i.e. Tb^{3+} decreases when it is co-doped with acceptor ion in zinc phosphate glass. This is further supported by Fig. 3 which shows the variation in donor intensity (1 wt% Tb^{3+}) with varying concentration of acceptor (Ho^{3+}) and shows a decrease in Tb^{3+} emission. The decrease in donor emission intensity overall indicates that there is non-radiative energy transfer from $^5D_4$ level of Tb^{3+} to Ho^{3+} ions[5]. Since the Ho^{3+} ion in zinc phosphate glass does not have any observable emission when excited by the 365 nm Hg source therefore, back transfer of energy from Ho^{3+} to Tb^{3+} is extremely low. A close look to the energy level diagram indicates that the levels of Ho^{3+} close to the emitting $^5D_4$ level of Tb^{3+} is $^8K_3$. Therefore, the excitation energy of Tb^{3+} ion is transferred to $^8K_3$ level of Ho^{3+}. The decay time of $^5D_4$

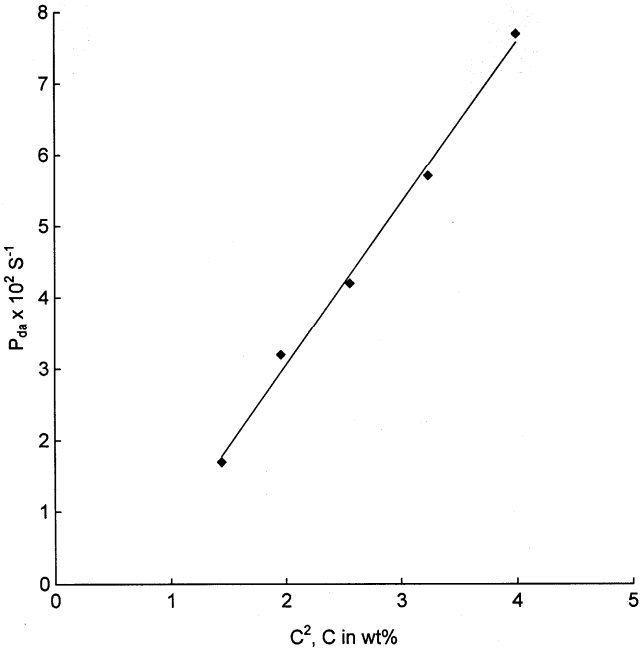

Fig. 4 — Variation of energy transfer probability (P_{da}) with square of donor + acceptor concentration

Table 1 — Effect of acceptor concentration on energy transfer efficiencies, probabilities and average donor-acceptor distances for Tb^{3+}-Ho^{3+} system at donor concentration 1 wt %

C_{donor} (wt %)	$C_{acceptor}$ (wt %)	D_{D-A} (nm; ±0.1)	I_{do} (±1)	I_d (±1)	η (±0.05)	$P_{da}\times10^3$ (s^{-1} ± 0.05)
1.0	0.2	2.26	70	49	0.30	0.17
	0.4	2.15		39	0.44	0.32
	0.6	2.06		34	0.51	0.42
	0.8	1.98		29	0.59	0.57
	1.0	1.91		24	0.66	0.77

where C_{donor} is the donor concentration; $C_{acceptor}$ the acceptor concentration; D_{D-A} the average donor-acceptor distance; I_{do} the donor intensity in the absence of acceptor; I_d the donor intensity in the presence of acceptor; η the energy transfer efficiency ($=1-I_d/I_{do}$); and P_{da} is the energy transfer probability [$=(1/\tau_0)(I_{do}/I_d - 1)$].

level of terbium ion is quite large (τ=2.5 ms) and hence, this level have enough time to transfer its energy to $^8K_3$ level of Ho^{3+}.

The linear dependence of energy transfer probabilities (P_{da}) on the square of the donor + acceptor concentrations (Fig. 4) is attributed to because of dipole-dipole interaction between donor and acceptor[5]. This fact is, further, supported by the fact that the average donor-acceptor separation which varies from 1.91 to 2.26 (Table 1) and falls in the range of electric dipole interaction between donor and acceptor ions[1, 2].

The critical transfer distance (R_0), at which the energy transfer probability is equal to the radiative transition probability, in our system is 2.08 nm which can be compared with those obtained by Joshi *et al.*[9,11] for Tb-Er [1.59 nm] and Eu-Er [2.01 nm] in zinc phosphate glass.

In the present study, the energy transfer by exchange mechanism is not possible as it needs a donor-acceptor ion separation of about 0.3-0.4 nm with considerable overlap of wave functions[3].

4 Conclusions

Non-radiative energy transfer from Tb^{3+} to Ho^{3+} occurs in zinc phosphate glass. Electric dipole-dipole interaction is mainly responsible for the energy transfer from Tb to Ho.

References

1 Forster Th, *Ann Phys*, 2 (1948) 55.
2 Dexter D L, *J Chem Phys,* 21 (1953) 836.
3 Inokuti M & Hirayama F, *J Chem Phys*, 43(6) (1965) 1978.
4 Uitert van L G & Johnson L F, *J Chem Phys,* 44 (1966) 3514.
5 Fong F K & Diestler D J, *J Chem Phys,* 56 (1972) 2875.
6 Joshi B C, *J Non-Cryst Solids*, 180 (1995) 217.
7 Liu Y, Yang Y, Qian G, Wang Z, Wang M Q, *Material Sci & Eng B,* 137 (2007) 74.
8 Yamashita T & Ohishi Y, *Chem Phys Lett J Non-Cryst Solids,* 354 (2008) 1883.
9 Joshi B C, Upreti D K, Dhondiyal C C & Khulbey B, *Indian J Pure & Appl Phys*, 46 (2008) 706.
10 Dhondiyal C C, Ph D Thesis, Kumaun University Nainital, India, 2008
11 Joshi B C, Dhondiyal C C, Upreti D K & Khulbey B, *Indian J Pure & Appl Phys,* 44 (2006) 811.